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A Simple Explanation on The Nobility of Gold Comparing to Other Metals: A First-Principles Study

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Abstract: We evaluate the reactivity of the Au surface towards H_2 and compared the reactivity with Ag, Cu, and Pt surfaces. The reactivity is represented by the H_2 dissociation energy over each surface. Their dissociation energies were calculated based on DFT calculation with PBE functional and PAW pseudopotential. The calculation results show that the Pt surface is the most reactive, followed by the Cu, Ag, and Au surfaces. The PDOS illustrates the d-band center is above Fermi level only on the Pt surface which indicates that it is the most reactive towards H_2. The adsorbate charge shows that Cu donates the most electrons, trailed by Ag and Au. This study concludes that Au surface is the most inert among the other three metals. This inertness is a characteristic that defines a noble metal.

Keywords: Density Functional Theory, noble metal, adsorption energy, molecule–surface interaction, transition metal reactivitv. d-band center. electron donation

1. Introduction

It has been known that Au is the noblest of all metals. [1,2] To put it simply, the nobleness of Au is shown from its inertness. Au is hard to react with molecules like O_2 and H_2O [3,4], which by and large react effectively with other transition metals. On the other hand, Au can still form stable alloys with other metals. [5] Moreover supported Au surfaces show a high catalytic activity for carbon monoxide oxidation, water gas shift, and hydrogenation reaction.

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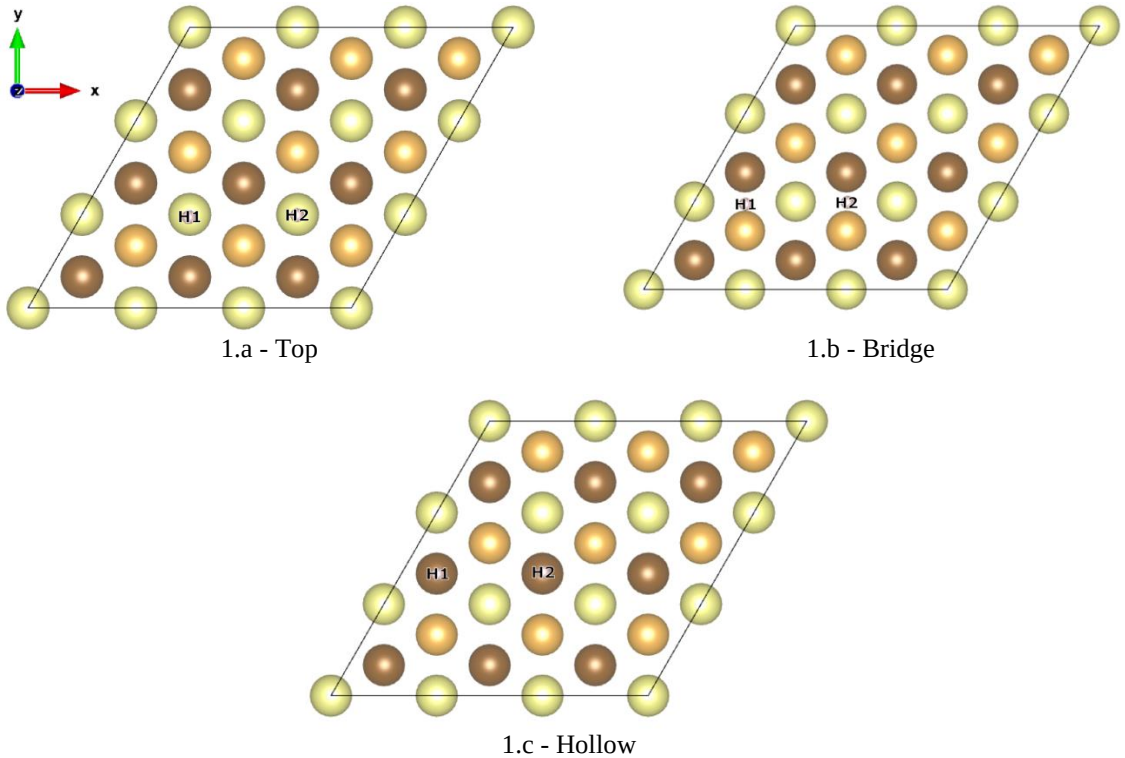
[4,6-8] These makes Au reactivity intriguing to investigate. Theoretical study of the nobleness of Au has been done comprehensively by Hammer. [1] Hammer compared the nobleness of Au with other metals, namely Cu, Pt, and Ni, based on the H_2 dissociation reaction on the surfaces. Hammer concluded that calculation results based on density functional theory (DFT) of activation barrier and adsorption energy are proportional to (1) number of filled antibonding states and (2) orbital overlap magnitude between surface and adsorbate. The combination of these two factors determines the strength of the adsorbate and metal interactions. In the present study, the nobleness of Au is explained in a simpler manner. We compared the reactivity of Au with other transition metals in the same group (Ag and Cu) and in a different group (Pt). The reactivity is studied from H_2 dissociation energy on the surfaces, without considering the activation barrier. Even so, Grimme's semiempirical correction [9] is incorporated into the DFT calculation to take the dispersion effect between adsorbate and metal. Other than analyzing DOS (bonding and antibonding states) as Hammer did, we additionally analyzed the atomic charge density to explain the reactivity levels of these metals.

2. Methodology

We used Au, Ag, Cu, and Pt surfaces with Miller index (111). The lattice constants for these surfaces are 4.07Å [10], 4.08Å [11], 3.68Å [12], and 3.94Å [13] respectively. Slab model of the surfaces is constructed using 27 atoms which are divided into three layers. Optimization is done on the top layer while the latter two layers are fixed to maintain the bulk structure. Optimization calculation is done before and after the H_2 dissociated above the surfaces. Before dissociation, H_2 is placed 6 Å on the normal direction of the surfaces. After dissociation, those H atoms are placed 1 Å on top, bridge, and hollow positions of the surfaces (see Figure 1). However, H atoms (and the metal atoms of the uppermost surface layer) are free to move during optimization. This procedure is typical for DFT calculation on molecule adsorption on surface. [14-18] Dissociation reaction energy is the difference between the energy of the H_2—surface system before and after dissociation.



1.a - Top

1.b - Bridge

1.c - Hollow

Fig. 1 - Top view of H atoms position after being dissociated on the surfaces. Bright circles are the metal atoms of the uppermost layer, while darker circles denote metal atoms of the deeper layers

The optimization calculation is done based on DFT using Quantum ESPRESSO software. [19,20] For that, approximation of exchange-correlation functional is done using PBE functional. [21] PAW pseudopotential is applied to model the core electron dynamics. [22] Dispersion effect are considered using Grimme's semiempirical correction. [9] We use the k-point Monkhors-Pack [23] whose grid size we obtained through convergence test along with two other parameters: the magnitude of kinetic energy cutoff for wavefunction, and the vacuum height. The results of the convergence test are presented in Table 1. For Self-Consistent Field (SCF) calculation, this study uses force threshold for geometric optimization with a magnitude of 10^{-3} Ry/Bohr while the energy threshold with a magnitude of 10^{-6} Ry.

In essence, DOS are also analyzed by projecting it onto atomic orbitals and calculating the atomic charge density using Bader Charge Analysis version 1.04. [24]

Table 1 - Cut-off energy (E_{cut}), k-point, and vacuum height (Vac.) for each surface obtained through convergence test

Surface	E_{cut} (eV)	k-point	Vac. (Å)
Au(111)	510	9	12
Ag(111)	570	8	11
Pt(111)	490	5	12
Cu(111)	510	8	11

3. Results and Discussion

Table 2 gives information about the adsorption configuration of H_2 after dissociated on the Au (111), Ag (111), Cu (111), and Pt (111) along with their energies. For Au (111) and Pt (111), the H atoms can be adsorbed on top, bridges, and hollow. Whereas in Ag (111) and Cu (111), H atoms can only be adsorbed on bridges and hollows, with hollow being the majority of adsorption sites. The energy difference between configurations indicates that H atoms tend to be adsorbed at the hollow sites for Au (111), Ag (111), and Cu (111), and the top sites for Pt (111). Figure 2 shows the difference in dissociation energy on each surface. The most positive H_2 dissociation energy is in Au (111), followed by Ag (111), Cu (111), and Pt (111). H_2 dissociation above Au (111) and Ag (111) are endothermic while on Cu (111) and Pt (111) are exothermic. This means, energetically, the dissociation reaction of H_2 above Au (111) and Ag (111) are harder compared to Cu (111) and Pt (111).

Table 2 - Adsorption configuration of dissociated H_2 (H1, H2), their separation distance (*d*) in Å, and the energy of H_2–surface system (E) in eV. The adsorption sites of those H atoms on top, bridge, and hollow are represented by T, B, and H. The energy is relative to the site with the most negative energy value

No.	Au (111)			Ag (111)			Cu (111)			Pt (111)		
	H1,H2	*d*	*E*	H1,H2	*d*	*E*	H1,H2	*d*	*E*	H1,H2	*d*	*E*
1.	T, T	3.36	0.42	H,B	3.08	0.00	H,B	2.67	0.00	T,T	2.88	0.00
2.	B, B	3.33	0.05	H,H	3.07	0.01	H,H	2.66	0.00	B,B	2.84	0.22
3.	H, H	3.36	0.00							H,H	2.87	0.27

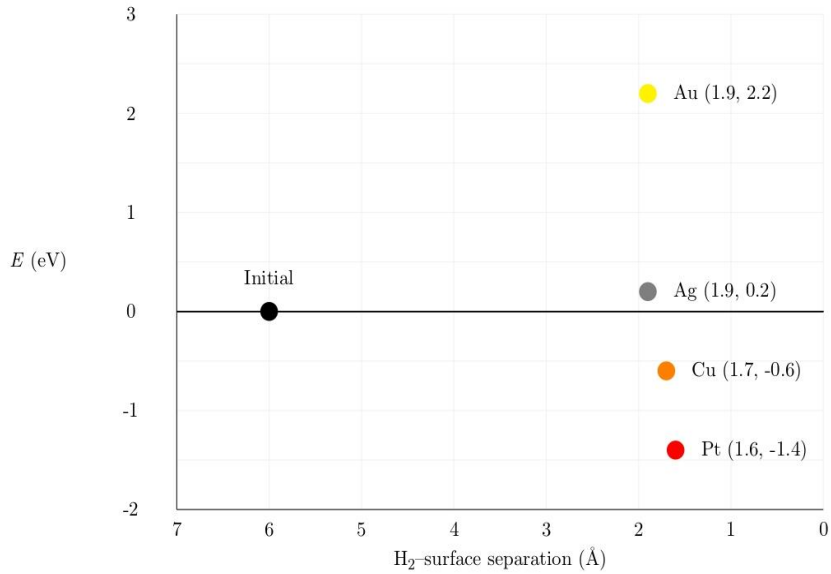


Fig. 2 - H_2–surface energy. The energy is relative to the initial state, when H_2 is located 6Å from the surface. In the final state, the H_2 is dissociated

Figure 3 shows the orbital interaction between Au (111) surface and the adsorbed H atoms. Similar interactions also happen for Ag (111), Cu (111), and Pt(111) surfaces. This shows that H undergoes chemisorption on these surfaces. Figure 4 shows the DOS from the H_2-surface system which are projected against the 1s H and d-band surfaces. The PDOS for 1s H orbital shows bonding and antibonding states from the interaction with the d-band surface. The bonding state is found to be the most dominant and formed below the energy value of -5 eV. The antibonding state is formed around the Fermi level. For Au (111), Ag (111), and Cu (111), the antibonding state is on the left side of the Fermi level, while for Pt (111), it is the other way around. The filling of the antibonding state for Au (111), Ag (111), and Cu (111) by electrons produces a repulsive force between H and these surfaces which results in their higher energy compared to Pt (111).

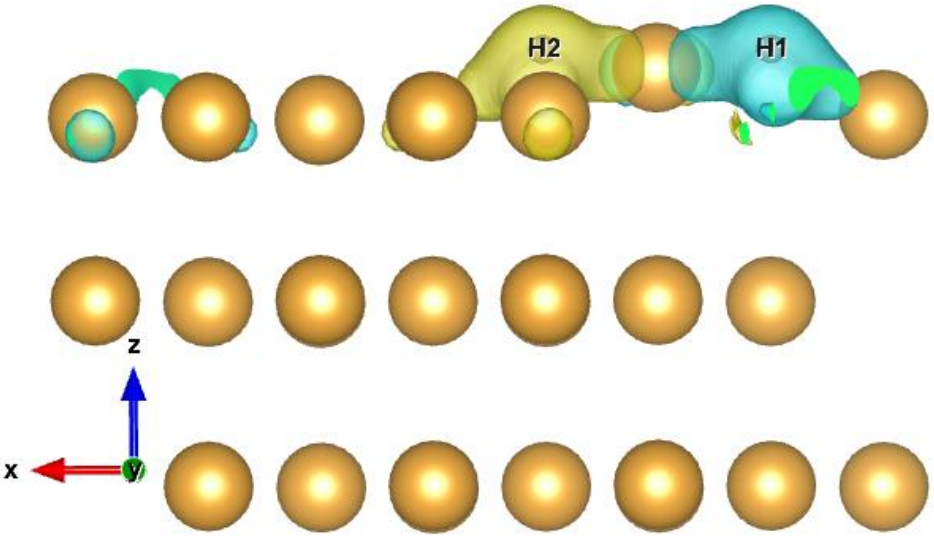


Fig. 3 - Isosurface molecular orbital of H_2–Au on an energy level of −7.78 eV (relative to Fermi energy) and isovalue 0.05. Each blue and yellow color shows positive and negative phases respectively

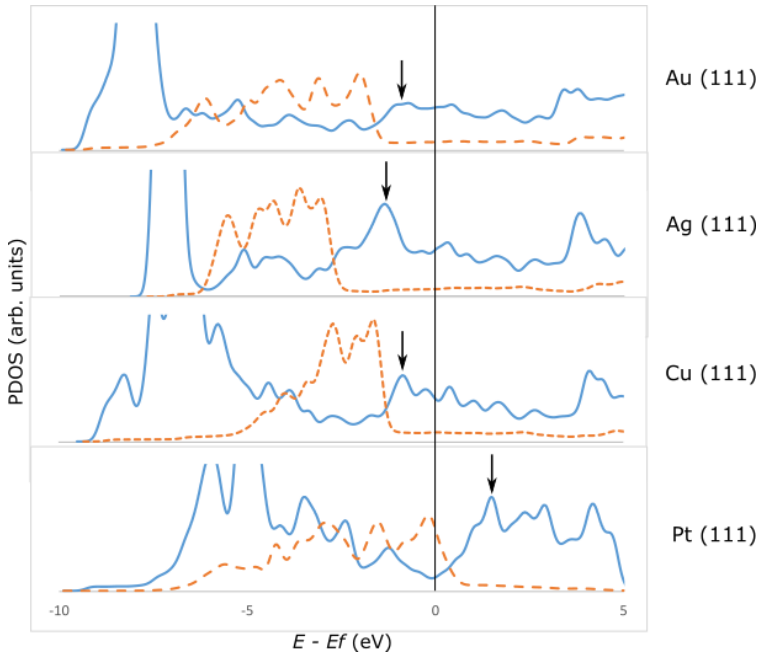


Fig. 4 - Solid line: Density of States (DOS) of H_2–surface projected onto the 1s H orbital. Dashed line: DOS clean surface projected onto d-bands. The arrows indicate the antibonding states between 1s H and d-bands surface. The energy is relative to Fermi energy

The position of the antibonding state is in line with the position of d-band surface. The d-bands of Au(111), Ag(111), and Cu(111) are totally located on the left side of the Fermi level, while a part of Pt(111) d-band is located on

the right side of the Fermi level. As a result, it can be known from the d-band position that Pt (111) is more reactive compared to Cu (111), Ag (111), and Au (111). On the periodic table of elements, Au, Ag, and Cu are in Group 1B while Pt is in Group 8B. Hence, the reactivity of metals in various groups can be explained based on their d-band position towards Fermi level. Table 3 shows the charge of the adsorbed H atoms. Au (111), Ag (111), Cu (111), and Pt (111) altogether donate their electrons to the H atoms, causing the H atoms to have a negative charge. Even so, it can be known from the charge that Cu (111) donates the most electrons, followed by Ag (111), Au (111), then Pt (111). The order of the ability to donate electrons by Cu, Ag, and Au are in the same trend with H_2 dissociation energy for those metals (Figure 1). The three metals are in the same group on the periodic table of elements. Henceforth, the reactivity of metals on a particular group can be explained based on the ability to donate electrons to the adsorbate.

Table 3 - Charges of the adsorbed hydrogens

No.	Surface	H1	H2
1.	Au(111)	-0.082	-0.062
2.	Ag(111)	-0.208	-0.205
3.	Pt(111)	-0.302	-0.307
4.	Cu(111)	-0.041	-0.040

4. Conclusion

We have successfully evaluated the reactivity of Au, Ag, Cu, and Pt metals based on the H_2 dissociation energy on those metals. The order from least reactive to most reactive is Au, Ag, Cu, and Pt. We have explained the reactivity order of these metals based on (1) the d-band position of the metal to Fermi level and (2) its ability to donate electrons to the adsorbate. The d-band of (Pt) is partially filled with a higher reactivity compared to metals in Group 1B (Au, Ag, and Cu) whose d-bands are fully filled. Within the same group, the ability of a metal to donate its electron to adsorbate is proportional to its reactivity. Cu donates the most electrons to H_2, followed by Ag, then Au. These results corroborate the reactivity order of those three metals in Group 1B.

Author Contribution

Conceptualization, methodology: Febdian Rusydi. Investigation: Eduardus O. Kristianto. Formal Analysis: Eduardus O. Kristianto and Samuel E. P. P. Masan. Project administration: Wahyu A. E. Prabowo. Supervision: Febdian Rusydi, Muhammad Iqbal, Irzaman, Widagdo S. Nugroho. Writing--original draft: Eduardus O. Kristianto. Writing--review \& editing: Febdian Rusydi, Wahyu A. E. Prabowo, Samuel E. P. P. Masan.

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